(19) Japanese Patent Office (JP)

(12) Patent Disclosure (Kokai) Gazette (A)

(11) Patent Application Disclosure: Hei 3-203901

(43) Disclosure Date: September 5, 1991

(51) International Classes		Identification Codes	Patent Office Internal Filing Numbers
C 08 F	2/26	MBV	7107-4J
B 01 F	17/52		6345-4G

Demand For Examination: Not demanded

Number of Claim Paragraphs: 1

([Original has] 4 pages)

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(54) Title Of The Invention: Dispersant For Emulsion Polymerization

(21) Patent Application: Hei 1-344218

(22) Application Date: December 19, 1989

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Specification

1. Title Of The Invention.

Dispersant For Emulsion Polymerization

2. Scope Of Patent Claim.

1. Dispersant for emulsion polymerization characterized in that it comprises a salt of a polystyrene sulfonic acid with a sulfonation rate of 80 to 95%, where the sulfonated polystyrene has an average molecular weight of 2000 to 100000.

3. Detailed Explanation Of The Invention.

(Field Of Industrial Utilization)

The present invention relates to a new anionic dispersant for emulsion polymerization used in the manufacture of latex.

(Prior Technology)

Non-ionic surfactants have been used priorily as dispersants for emulsion polymerization, including anionic surfactants such as straight chain alkyl sulfates, straight chain alkylbenzene sulfonates, polyoxyethylenealkylether sulfates, fatty acid salts and resin acid salts, and non-ionic surfactants such as polyoxyethylenealkylethers,

polyoxyethylenealkylphenylethers, polyoxyethylene fatty acid esters and pluronic type surfactants.

Emulsion polymerization generally makes mixtures in water of difficultly soluble types of ethylenic unsaturated monomers or conjugated diene monomers, either singly or in mixtures, and polymerizes in water soluble media. Emulsifiers are required not only as means for advancing the polymerization smoothly, but also for imparting stability to the emulsion formed.

However, with these surfactants there are many cases of latex having insufficient stability, for example emulsion polymerization of latex such as SBR, NBR and CR gives insufficient stability, leading to problems of condensates tending to form during polymerization and a tendency to gel during storage. In this regard Japanese Patent Disclosure Sho 49-37118 and Japanese Patent Disclosure Sho 55-142019 offered formalin condensates of alkylnaphthalene sulfonic acid and naphthalene sulfonic acid as agents functioning as emulsifiers for polymerization and agents also functioning as dispersants.

Again, Japanese Patent Publication Sho 61-40241 publishes the fact that chloroprene rubber with low mold stains when there is an excess of sulfur in the mold can be obtained by making chloroprene rubber by polymerizing chloroprene in alkaline aqueous emulsified salt under presence of resin acid derivatives and polystyrene sulfonic acid salts.

Further, Japanese Patent Disclosure Hei 1-268704 offers a salt of sulfonation degree 0.45 to 0.75 polystyrene sulfonic acid obtained by sulfonating polystyrene with an average molecular weight from 1000 to 100000 as measured by the GPC method for use as a dispersant for emulsion polymerization.

However in these cases, even if the dispersability is good, there tends to be deterioration of system stability at time of polymerization, and there is the problem of foaming during polymerization.

(Problems To Be Resolved By The Invention)

The present invention is one that offers a dispersant for emulsion polymerization that suppresses foaming at time of emulsion polymerization with no harm to polymerization, and while raising the stability of the latex formed, imparts no harmful effects to the properties or qualities of the polymer.

(Construction Of The Invention)

The dispersant for emulsion polymerization of the present invention is characterized in that it comprises a salt of a polystyrene sulfonic acid with a sulfonation rate of 80 to 95%, where the sulfonated polystyrene has an average molecular weight of 2000 to 100000.

The present invention will be explained in further detail next.

The polystyrene used in the present invention is obtained by radical polymerization or cation polymerization of styrene

following conventional methods, and 1000 to 50000 molecular weight polymer can be used.

In regard to the method of sulfonating the polystyrene obtained, it is satisfactory to do the sulfonation following conventional methods by diluting the polystyrene in an inert solvent in a sulfonation reagent, and using sulfonation reagents such as SO^3, fuming sulfuric acid and sulfuric acid. This sulfonation chemical is first neutralized with an alkali such as sodium hydroxide or potassium hydroxide, or with an amine, and then by removing the solvent the sulfonic acid salt can be obtained. [Revision made here.]

Modification of the sulfonation rate can be controlled by modifying the mol ratio of the raw materials polystyrene and sulfonation reagent at time of sulfonation, to set the sulfonation rate at 80 to 95%. A sulfonation rate lower than 80% is undesirable because of foaming during polymerization, and if it is over 95% it is undesirable because it becomes too hydrophilic and worsens system stability during polymerization.

The sulfonation substance of the polystyrene of the present invention can be manufactured even with styrene copolymers having styrene sulfonic acid or styrene sulfonic acid salt, and in these cases the mol ratio of the styrene sulfonic acid (salt) and the styrene will be in the range from 80: 20 to 95: 5.

The molecular weight of the sulfonation chemical in the polystyrene is 2000 to 100000 as measured by the GPC method (gel permeation chromatography), and preferably 5000 to 50000. At less than 2000 molecular weight, there is insufficient adsorption on the latex formed in the emulsion polymerization and dispersability deteriorates, while more than 100000 molecular weight is undesirable because viscosity rises during polymerization.

Emulsion polymerization employing dispersants used for emulsion polymerization following the present invention can be done by known methods. For example, 100 parts by weight of monomer is given additions of 60 to 500 parts by weight of water, 0.5 to 10 parts by weight of emulsifier used for emulsion polymerization, 0.5 to 10 parts by weight of the present invention's dispersant used for emulsion polymerization, a suitable amount of polymerization initiator, and finally inorganic salts and chain transfer agents as required, to obtain the object rubber type or other resin type high molecular latex emulsion. The monomers used here include known monomers such as chloroprene, 1-chlorobutadiene, 2,3-dichlorobutadiene, butadiene, 2-cyanobutadiene, styrene, acrilonitrile, methacrylic acid alkyl ester and acrylic acid alkyl ester. These monomers can be used singly or in mixtures as required.

(Effect Of The Invention)

Following the present invention, when a salt of a polystyrene sulfonic acid with a sulfonation rate of 80 to 95%, where the sulfonated polystyrene has an average molecular weight of 2000 to 100000, is used as a dispersant for emulsion polymerization when manufacturing a latex emulsion by emulsion polymerization, it is possible to polymerize without bringing about problems of foaming and deterioration of system stability during polymerization. Further, it is possible to do the manufacturing without imparting effects on the properties of the latex or on the manufactured product, so that it is highly suitable for industrial manufacturing of latex emulsion.

(Examples)

In a reaction vessel furnished with a thermometer, stirrer, reflux cooler and drop funnel, the following were placed and given nitrogen substitution: 100 parts by weight of chloroprene, 2.0 parts by weight of uniform rosin acid, 0.4 weight percent of caustic soda, 1.0 parts by weight of dispersant used for emulsion polymerization as indicated in Table 1 below, 0.25 parts by weight of dodecyl mercaptan and 100 parts by weight of water. Then an aqueous solution of 0.5 wt% potassium persulfate was added to the reaction vessel dropwise at 1.0 weight percent as a catalyst, and polymerization was carried out at 40 °C under nitrogen reflux.

t-Butyl cathecol and phenothiazine were added to the reaction vessel at 0.01 parts by weight each at a polymerization conversion rate of 70%, and the polymerization was stopped. The latex emulsion obtained was evaluated for condensation, foaming and coloring as shown below, with the results presented in Table 1.

(1) Condensation

The emulsion manufactured was filtered in an 80 mesh sieve, the remnant after filtering was washed with water and dried to obtain the condensate, and the wt% relative to the starting monomer was taken as the condensation.

(2) Foaming

The emulsion obtained was taken as a 40 cc sample in a 100 cc Epton tube, and after shaking 10 times with a circular motion for about 5 seconds, the foam volume was calculated based on the following.

O: Foam volume 0 to 1 cc

Δ: Foam volume 1 to 3 cc

X: Foam volume over 3 cc

(3) Coloring

Estimated by visual appearance.

Table 1

表－1

		乳化重合用分散剤	分子量 (Mw)	スルホン化率 (%)	凝集性	発泡性	着色性
実施例	1	ポリスチレンスルホン酸Na	2000	80	0.51	○	無し
	2	ポリスチレンスルホン酸Na	7000	90	0.29	○	無し
	3	ポリスチレンスルホン酸Na	15000	88	0.30	○	無し
	4	ポリスチレンスルホン酸Na	30000	93	0.33	○	無し
比較例	1	ポリスチレンスルホン酸Na	7000	98	3.36	○	無し
	2	ポリスチレンスルホン酸Na	7000	70	0.34	×	無し
	3	ポリスチレンスルホン酸Na	150000	93	増粘	－	－
	4	ポリスチレンスルホン酸Na※1	10000	100	2.46	○	無し
	5	NSF－Na※2	－	－	0.35	○	着色

※1) スチレンスルホン酸Naを重合させたもの

※2) NSF：ナフタレンスルホン酸ホルマリン縮合物

[Column entries from left:]

Emulsion Polymerization Dispersant

Molecular Weight (MW)

Sulfonation Rate (%)

Condensation

Foaming

Coloring

[Japanese in first column:]

Example 1. Polystyrene sulfonic acid Na

Example 2. Polystyrene sulfonic acid Na

Example 3. Polystyrene sulfonic acid Na

Example 4. Polystyrene sulfonic acid Na

Comparative Example 1. Polystyrene sulfonic acid Na

Comparative Example 2. Polystyrene sulfonic acid Na

Comparative Example 3. Polystyrene sulfonic acid Na

Comparative Example 4. Polystyrene sulfonic acid Na *1

Comparative Example 5. Polystyrene sulfonic acid Na *2

[Japanese in fourth column:]

Thickening

[Japanese in sixth column:}

None

None

None

None

None

None

None

Coloration

[Notes:]

*1 Product of polymerizing styrene sulfonic acid Na.

*2 NSF: Nafthalene sulfonic acid formalin condensate.

[Start new document.]

Procedural Revision

March 25, 1991

TO: Director General Of The Patent Office Satoshi Uematsu, Esq.

1. Designation Of The Matter.

Patent Application Hei 1-344218

2. Title Of The Invention.

Dispersant For Emulsion Polymerization

3. Person Making The Revision.

Relation To The Matter:	Patent Applicant
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5. Object Of The Revision.

Detailed Explanation Of The Invention in the Specification.

6. Content Of The Revision.

(1) At line 6 on page 5 of the Specification, " ...sulfonic acid salt can be obtained. " is revised as follows.

"...sulfonic acid salt can be obtained.

The polystyrene sulfonic acid salt used can be such as alkali metal salt, alkali earth metal salt, organic amine salt and ammonium salt, for example such as sodium salt, potassium salt, calcium salt, magnesium salt and ammonium salt."

[Stamped impressions from top:]

Approved

[Seal of Patent Agent]

Patent Office, March 27, 1991, Application Section

Approved For Form

[Seal of Sekigawa]

End.